

Four 1-aryl-1*H*-pyrazole-3,4-dicarboxylate derivatives: synthesis, molecular conformation and hydrogen bonding

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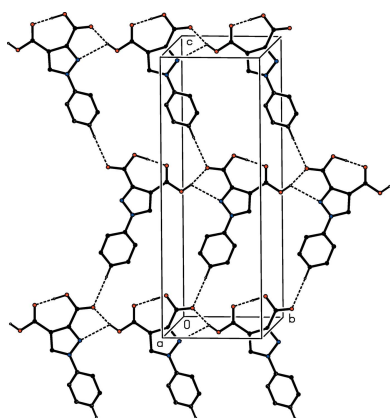
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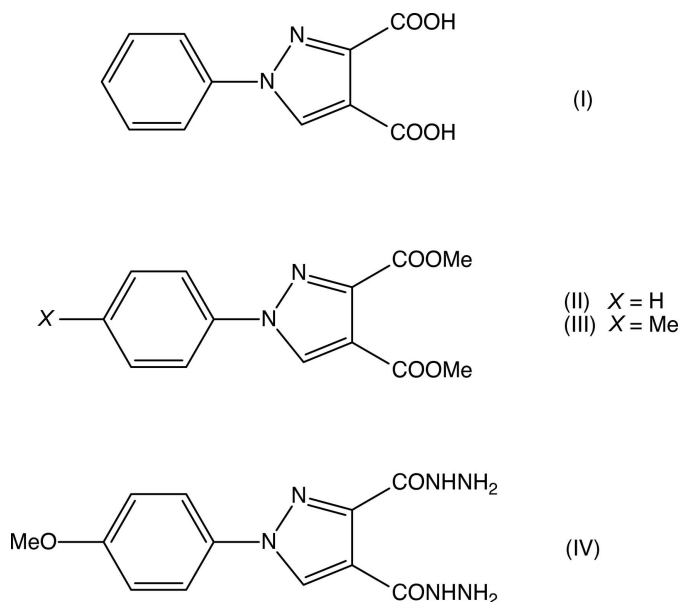
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Four 1-aryl-1*H*-pyrazole-3,4-dicarboxylate derivatives, one acid, two esters and a dicarbohydrazide have been synthesized starting from 3-aryl sydnones, and structurally characterized. There is an intramolecular O—H...O hydrogen bond in 1-phenyl-1*H*-pyrazole-3,4-dicarboxylic acid, C₁₁H₈N₂O₄, (I), and the molecules are linked into a three-dimensional framework structure by a combination of O—H...O, O—H...N, C—H...O and C—H... π (arene) hydrogen bonds. In each of the two esters dimethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate, C₁₃H₁₂N₂O₄, (II), and dimethyl 1-(4-methylphenyl)-1*H*-pyrazole-3,4-dicarboxylate, C₁₄H₁₄N₂O₄, (III), C—H...O hydrogen bonds lead to the formation of cyclic centrosymmetric dimers: in (III), one of the methoxy-carbonyl groups is disordered over two sets of atomic sites having occupancies 0.71 (2) and 0.29 (2). An intramolecular N—H...O hydrogen bond is present in the structure of 1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide, C₁₂H₁₄N₆O₃, (IV), and the molecules are linked into a three-dimensional framework structure by a combination of N—H...O, N—H...N, N—H... π (arene) and C—H...O hydrogen bonds. Comparisons are made with the structures of a number of related compounds.

1. Chemical context

Pyrazole derivatives have been shown to exhibit a wide range of biological activities including analgesic (Girisha *et al.*, 2010), anticonvulsant (Owen *et al.*, 1958), antimicrobial (Satheesha & Kalluraya, 2007; Asma *et al.*, 2018), antitumour (Park *et al.*, 2005), and insecticidal and larvicidal activity (Yang *et al.*, 2018). Pyrazole carboxylic acids and their derivatives are versatile precursors for the synthesis of numerous substituted analogues (Asma *et al.*, 2018; Devi *et al.*, 2018) and, with these considerations in mind, we have now synthesized a series of new pyrazole carboxylate derivatives as intermediates for the synthesis of new pharmacologically active products. Here we report the syntheses, and the molecular and supramolecular structures of four such compounds, namely 1-phenyl-1*H*-pyrazole-3,4-dicarboxylic acid (I), dimethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (II), dimethyl 1-(4-methylphenyl)-1*H*-pyrazole-3,4-dicarboxylate (III) and 1-(4-methoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (IV) (Figs. 1–4).





The products (II) and (III) and the intermediate ester (*B*) (Fig. 5) used in the formation of compound (IV) were all prepared using the 1,3-dipolar addition reaction between dimethyl acetylenedicarboxylate and the 3-arylsyndones [3-aryl-1,2,3-oxadiazol-3-ium-5-olates] (*A*), with loss of carbon dioxide in entropy-driven reactions (Huisgen *et al.*, 1962) (Fig. 5). Hydrolysis of the ester (II) gave the dicarboxylic acid (I), while hydrazinolysis of the ester (*B*) gave the dicarbohydrazide (IV). The sydnone precursors (*A*) were all prepared from the corresponding anilines *via* the substituted *N*-aryl-*N*-nitrosoglycines (Greco *et al.*, 1962; Fun *et al.*, 2010).

2. Structural commentary

The bond distances in compounds (I)–(IV) show no unexpected values: all are typical of their types (Allen *et al.*, 1987). However, the molecular conformations show some interesting features. In each of (I) and (IV), the two carboxy substituents on the pyrazole ring are nearly coplanar with this ring, as shown by the leading torsional angles (Table 1): this is almost certainly a consequence of the presence on an intramolecular

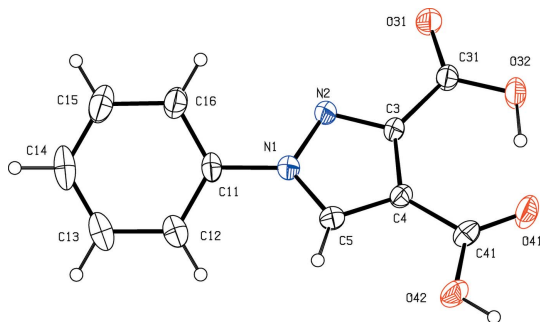


Figure 1
The molecular structure of compound (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

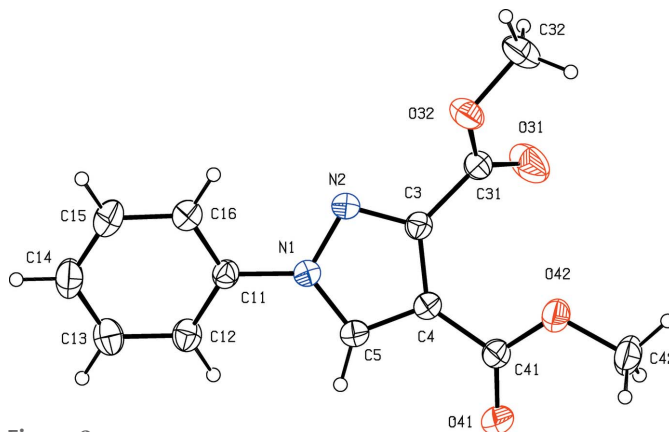


Figure 2
The molecular structure of compound (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

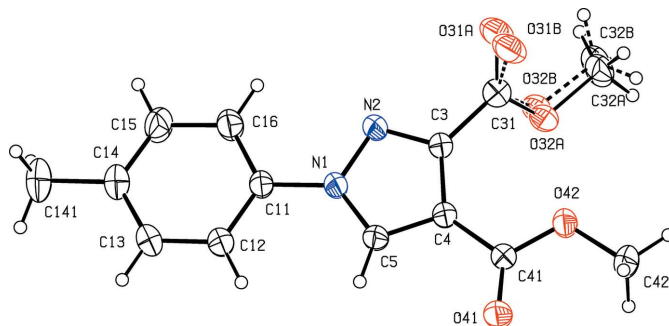


Figure 3
The molecular structure of compound (III) showing the atom-labelling scheme. The major disorder component, occupancy 0.71 (2), is drawn using full lines and the minor component, occupancy 0.29 (2), is drawn using dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

O—H...O in (I) and an intramolecular N—H...O hydrogen bond in (IV) (Table 2). In compounds (I) and (III), where such intramolecular interactions are not possible, the carboxyl groups at C3 are by no means coplanar with the pyrazole ring (Table 1), and in compound (III) the 3-methoxycarbonyl substituent is disordered over two sets of atomic sites having occupancies 0.71 (2) and 0.29 (2) in the crystal selected for

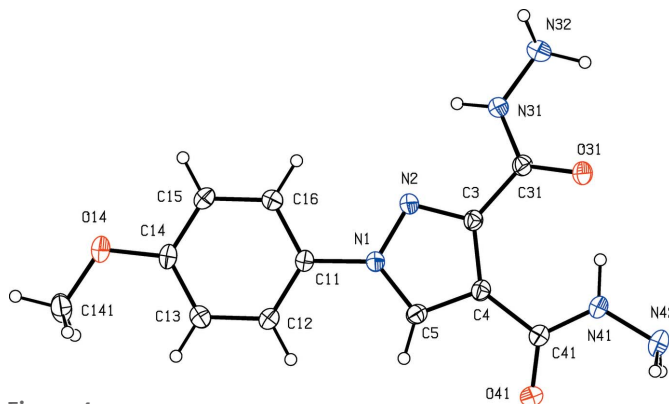


Figure 4
The molecular structure of compound (IV) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

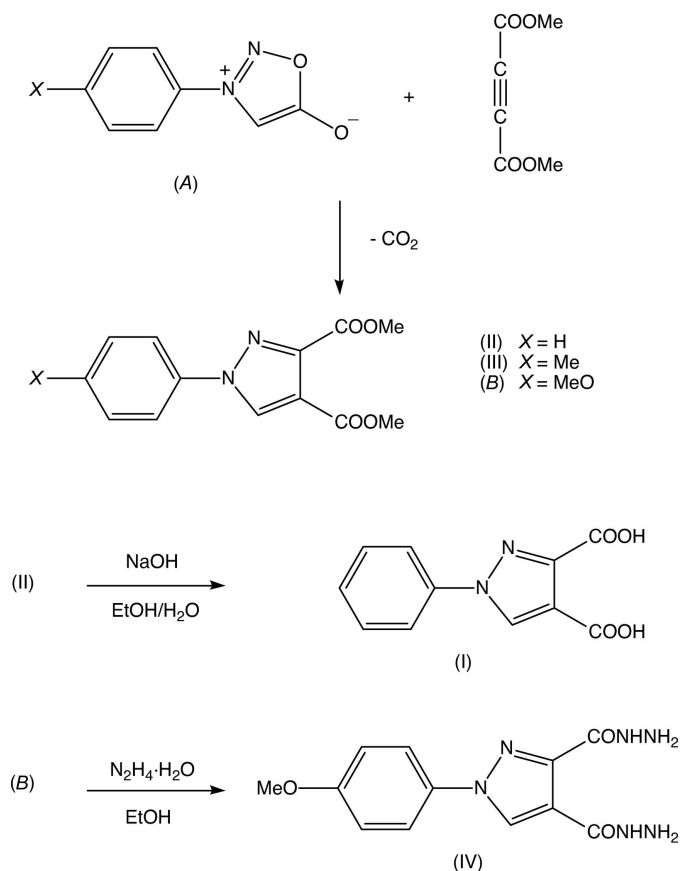
Table 1Selected torsional and dihedral angles ($^{\circ}$).

φ_1 represents the dihedral angle between the planes of the aryl and pyrazole rings and φ_2 represents the dihedral angle between the planes (C3,C31,O31A,O32A) and (C3,C31,O31B,O32B)

	(I)	(II)	(III)	(IV)
C4—C3—C31—O31	−178.0 (2)	44.8 (3)		−12.5 (4)
C4—C3—C31—O32	2.1 (4)	−135.9 (2)		
C4—C3—C31—O31A			−129.1 (9)	
C4—C3—C31—O31B			−96.6 (9)	
C4—C3—C31—O32A			57.5 (6)	
C4—C3—C31—O32B			71.6 (8)	
C4—C3—C31—N31				168.4 (2)
C3—C4—C41—O41	−2.5 (4)	−168.5 (2)	176.5 (2)	−169.0 (2)
C3—C4—C41—O42	178.0 (2)	12.8 (3)	−3.0 (3)	
C3—C4—C41—N41				9.8 (4)
φ_1	29.38 (8)	24.38 (12)	2.78 (12)	5.82 (13)
φ_2			22.7 (5)	

data collection: the orientations of the two disorder components are related to one another by a rotation about the C3—C31 bond of approximately 23° (Table 1). It may be noted here that the ketonic O atom O31 acts as a hydrogen-bond acceptor in each of (I) and (IV), but not in (II) and (III) (Table 2), and the disorder in (III) may be associated with this.

In each of (I) and (II), the planes of the aryl and pyrazole rings make much larger dihedral angles than these planes do

**Figure 5**
The synthetic routes to compounds (I)–(IV).

in (II) and (IV) (Table 1). This may be associated with the cooperative effect in (III) and (IV) of the C—H···O hydrogen bonds involving atoms C5 and C12 as donors (Table 2), whereas no such cooperation is found in the structures of (I) and (II).

3. Supramolecular features

The supramolecular assembly of compound (I) to form a three-dimensional framework structure depends upon four types of hydrogen bonds (Table 2), and the framework formation can readily be analysed in terms of one-dimensional sub-structures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). A combination of O—H···O and O—H···N hydrogen bonds, the latter rather weak, links molecules related by translation into a $C(6)C(7)[R_1^2(5)]$ (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) chain of rings running parallel to the [010] direction (Fig. 6). In the second sub-structure, molecules related by the c -glide plane at $y = 0.25$ are linked by a C—H···O hydrogen bond to form a simple $C(10)$ chain running parallel to the [001] direction, and the combination of these two chain motifs generates an almost planar sheet lying parallel to (100) in the domain $\frac{1}{4} < x < \frac{1}{2}$ (Fig. 6). Finally, two weak C—H··· π (arene) hydrogen bonds link this sheet to the adjacent sheets in the domains $0 < x < \frac{1}{4}$ and $\frac{1}{2} < x < \frac{3}{4}$, and in this way all of the (100) sheets are linked to form a three-dimensional framework structure.

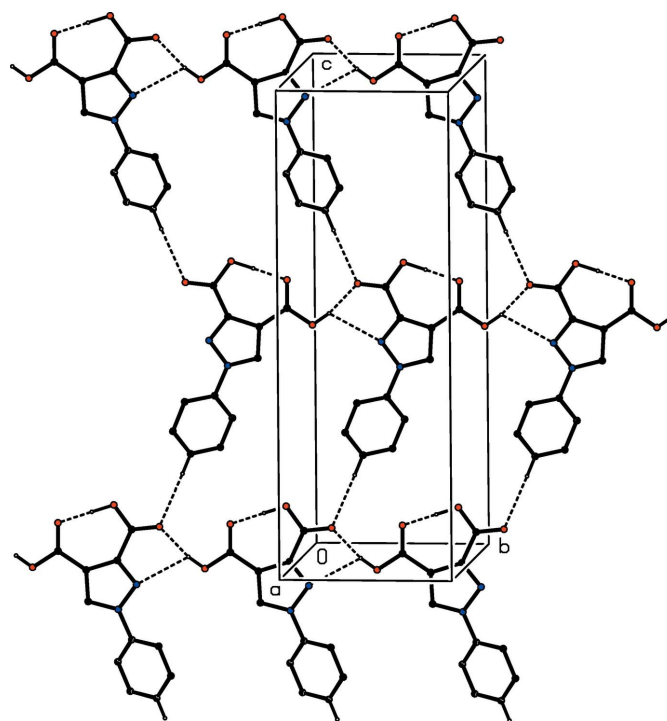
**Figure 6**
Part of the crystal structure of compound (I) showing the formation of a hydrogen-bonded sheet parallel to (100). Hydrogen bonds are shown as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms but not involved in the motifs shown have been omitted.

Table 2

Hydrogen bonds and short intermolecular contacts (Å, °).

Cg1 represents the centroid of the C11–C16 ring.

Compound	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)	O32–H32 \cdots O41	1.00 (3)	1.54 (3)	3.546 (2)	178 (2)
	O42–H42 \cdots O31 ⁱ	0.88 (3)	1.80 (3)	2.660 (2)	168 (3)
	O42–H42 \cdots N2 ⁱ	0.88 (3)	2.56 (3)	3.063 (3)	117 (2)
	C14–H14 \cdots O31 ⁱⁱⁱ	0.93	2.53	3.456 (3)	177
	C12–H12 \cdots Cg1 ⁱⁱⁱ	0.93	2.86	3.685 (3)	148
(II)	C15–H15 \cdots Cg1 ^{iv}	0.93	2.92	3.755 (3)	151
	C5–H5 \cdots O41 ^v	0.93	2.41	3.331 (3)	170
(III)	C5–H5 \cdots O41 ^{vi}	0.93	2.33	3.249 (3)	168
	C12–H12 \cdots O41 ^{vi}	0.93	2.43	3.352 (3)	173
(IV)	N31–H31 \cdots O31 ^{vii}	0.88 (2)	2.04 (2)	2.851 (3)	153 (2)
	N32–H32A \cdots O14 ^{viii}	0.97 (3)	2.58 (3)	3.256 (3)	127 (2)
	N32–H32B \cdots N42 ^{vii}	1.00 (2)	2.34 (3)	3.317 (3)	165 (2)
	N41–H41 \cdots O31	0.95 (3)	1.78 (3)	2.714 (3)	166 (2)
	N42–H42A \cdots O41 ^{ix}	0.95 (3)	2.21 (3)	3.120 (3)	162 (2)
	N42–H42B \cdots Cg1 ^x	0.83 (3)	2.85 (3)	3.442 (3)	130 (2)
	C5–H5 \cdots O41 ^v	0.93	2.40	3.314 (3)	166
	C12–H12 \cdots O41 ^v	0.93	2.44	3.354 (3)	168

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iv) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $-x, 1 - y, 1 - z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (viii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ix) $1 - x, 1 - y, -z$; (x) $-1 + x, y, -1 + z$.

By contrast, the supramolecular assembly in the ester (II) is extremely simple, with inversion-related pairs of molecules linked by C–H \cdots O hydrogen bonds (Table 2) to form a centrosymmetric $R_2^2(10)$ dimer (Fig. 7). A similar, but more complex centrosymmetric dimer is formed by the ester (III), where the same $R_2^2(10)$ motif as found in (II) is present, along

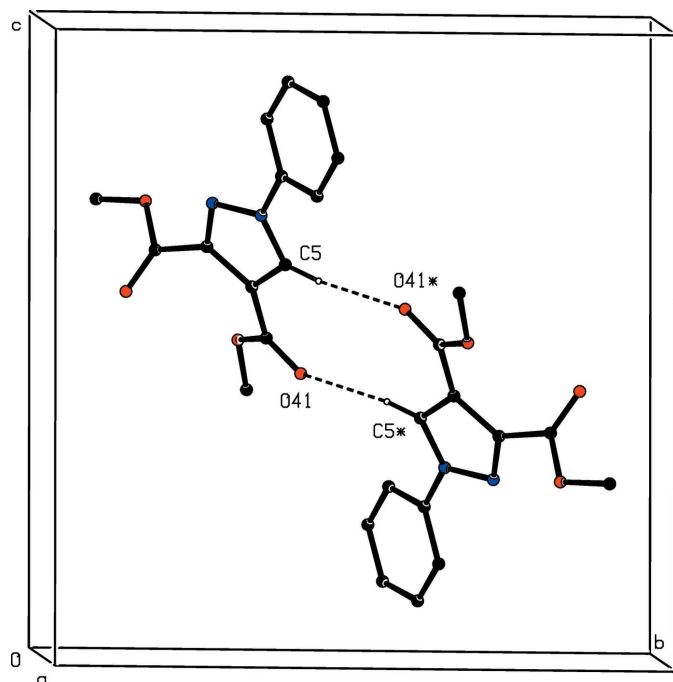


Figure 7

Part of the crystal structure of compound (II) showing the formation of a hydrogen-bonded $R_2^2(10)$ dimer. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, the H atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

with two flanking $R_2^1(7)$ rings within an outer $R_2^2(16)$ ring (Fig. 8). In neither (II) nor (III) are there any direction-specific interactions between adjacent dimers.

The supramolecular assembly in the hydrazide (IV) is the most complex of those reported here. A three-dimensional framework structure is built from four types of hydrogen bonds: N–H \cdots O, N–H \cdots N, N–H $\cdots\pi$ (arene) and C–H \cdots O (Table 2). As for (I), the assembly is readily analysed in terms of simpler substructures. The hydrogen bond involving atom H42A links an inversion-related pair of molecules into an $R_2^2(10)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, 0)$, and this finite, zero-dimensional sub-structure can be regarded as the basic building block of the overall structure, which can then be analysed in terms of the ways in which these dimers are linked together. The hydrogen bonds involving the atoms H31 and H32B directly link the reference dimer centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ to four similar dimers, centred at $(0, 0, -\frac{1}{2})$, $(0, 1, -\frac{1}{2})$, $(1, 0, \frac{1}{2})$ and $(1, 1, \frac{1}{2})$, so forming a sheet lying parallel to $(10\bar{1})$ (Fig. 9), which is reinforced by the N–H $\cdots\pi$ hydrogen bond (Table 2). The final sub-structure in the assembly of (IV) is one-dimensional: two C–H \cdots O hydrogen bonds link the basic $R_2^2(10)$ dimers into a chain of rings running parallel to the $[001]$ direction. Within this chain, two types of centrosymmetric

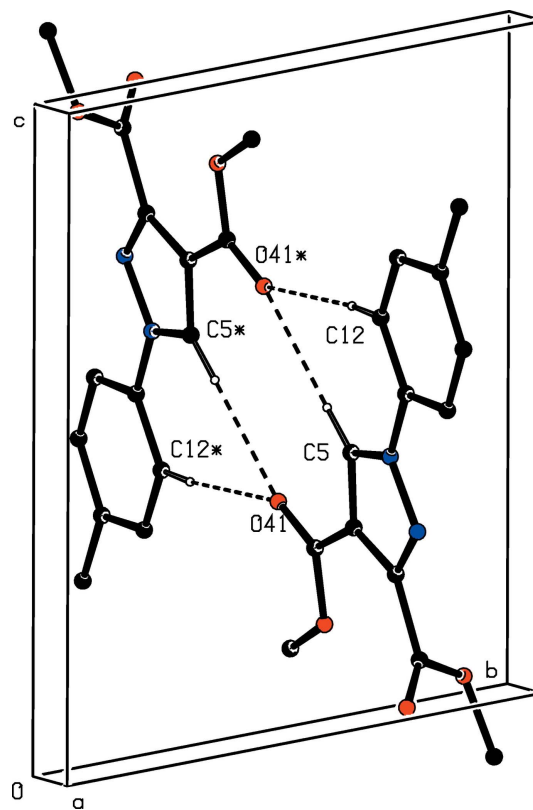


Figure 8

Part of the crystal structure of compound (III) showing the formation of a hydrogen-bonded dimer containing $R_2^1(7)$, $R_2^2(10)$ and $R_2^2(16)$ ring motifs. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, the minor disorder component and the H atoms not involved in the motifs shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position $(-x, 1 - y, 1 - z)$.

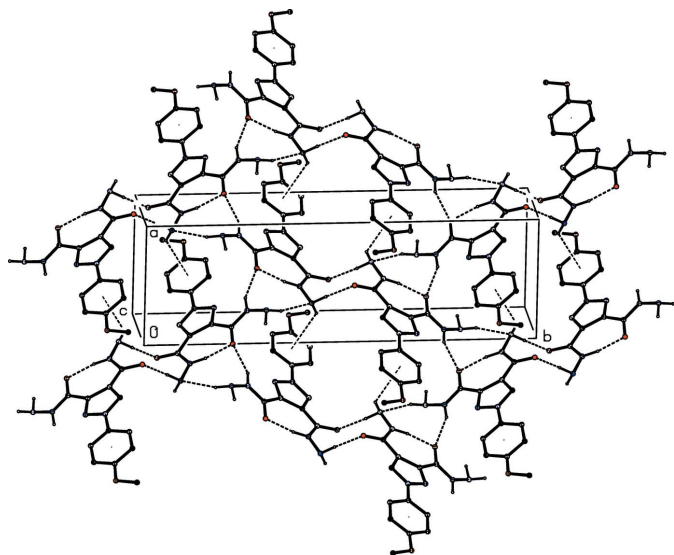


Figure 9

Part of the crystal structure of compound (IV) showing the formation of a hydrogen-bonded sheet lying parallel to (101) and built from N—H...O, N—H...N and N—H... π (arene) hydrogen bonds. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, the H atoms bonded to C atoms have been omitted.

$R_2^2(10)$ ring can be identified, one containing N—H...O hydrogen bonds and the other containing C—H...O hydrogen bonds, along with $R_2^1(7)$ rings (Fig. 10).

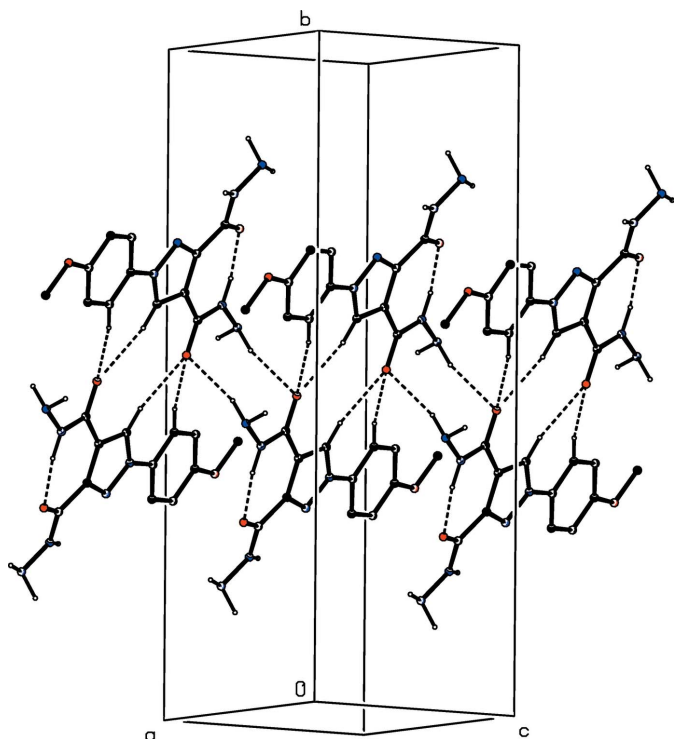


Figure 10

Part of the crystal structure of compound (IV) showing the formation of a hydrogen-bonded chain of rings parallel to [001] and built from N—H...O and C—H...O hydrogen bonds. Hydrogen bonds are shown as broken lines and, for the sake of clarity, the H atoms bonded to C atoms but not involved in the motifs shown have been omitted.

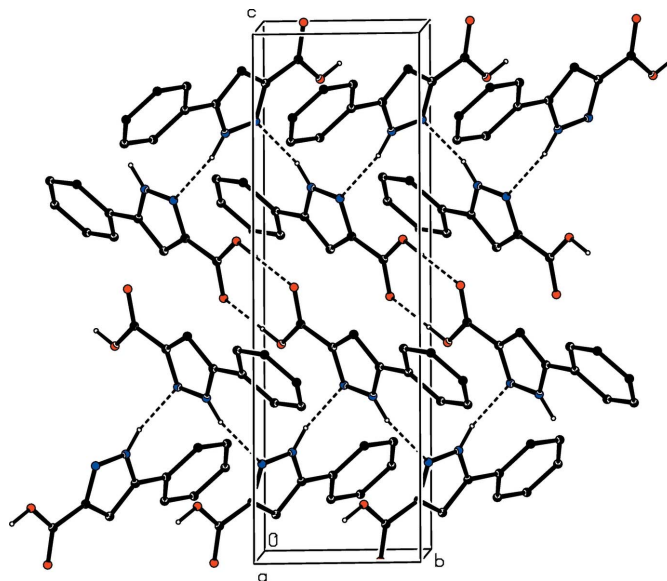


Figure 11

Part of the crystal structure of 3-phenyl-1*H*-pyrazole-5-carboxylic acid showing the formation of a sheet of $R_2^2(8)$ and $R_6^6(28)$ rings lying parallel to (100): hydrogen bonds are shown as dashed lines. The original atomic coordinates (Zhang *et al.*, 2007) have been used and, for the sake of clarity, the H atoms bonded to C atoms have all been omitted.

4. Database survey

It is of interest to compare briefly the structures of compounds (I)–(IV) reported here with those of some related compounds. In dimethyl 1-(3-chloro-4-methyl)-1*H*-pyrazole-3,4-dicarboxylate, which differs from (III) only in the presence of the additional 3-chloro substituent, there are again two C—H...O hydrogen bonds in the structure, involving exactly the same pair of C—H bonds as in (III), but here the molecules are linked into a $C(5)C(8)[R_2^1(7)]$ chain of rings, rather than into cyclic dimers (Thamotharan *et al.*, 2003). The esters dimethyl 5-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (Li *et al.*, 2014) and dimethyl 5-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (Alizadeh *et al.*, 2010), which carry an additional substituent in the pyrazole ring, are isostructural, and the molecules are linked by C—H...O hydrogen bonds to form simple chains.

The structures of several esters derived from 1-substituted-1*H*-pyrazole-3,5-dicarboxylic acids have been reported, including dimethyl 1-(2-cyanobenzyl)-1*H*-pyrazole-3,5-dicarboxylate (Xiao & Zhao, 2009), dimethyl 1-(4-cyanobenzyl)-1*H*-pyrazole-3,5-dicarboxylate (Yao *et al.*, 2009) and dimethyl 1-cyanomethyl-1*H*-pyrazole-3,5-dicarboxylate (Qu, 2009). There are no significant intermolecular interactions in either of the benzyl derivatives, but the inversion-related pairs of molecules of the 1-cyanomethyl compound are linked by C—H...O hydrogen bonds to form centrosymmetric $R_2^2(10)$ dimers.

In each of 1-benzyl-3-phenyl-1*H*-pyrazole-5-carboxylic acid (Tang *et al.*, 2007) and 1-cyclohexyl-5-(4-methoxyphenyl)-1*H*-pyrazole-4-carboxylic acid (Fun *et al.*, 2011), inversion-related

Table 3
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	C ₁₁ H ₈ N ₂ O ₄	C ₁₃ H ₁₂ N ₂ O ₄	C ₁₄ H ₁₄ N ₂ O ₄	C ₁₂ H ₁₄ N ₆ O ₃
<i>M_r</i>	232.19	260.25	274.27	290.29
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2₁/n</i>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P2₁/n</i>
Temperature (K)	296	296	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.164 (2), 7.4692 (9), 21.173 (3)	5.9000 (4), 14.5273 (12), 14.8726 (12)	7.6546 (5), 8.0959 (5), 11.3065 (6)	7.6030 (6), 22.6605 (19), 7.6751 (7)
α , β , γ (°)	90, 90, 90	90, 98.867 (3), 90	78.988 (3), 85.527 (3), 87.548 (4)	90, 102.284 (3), 90
<i>V</i> (Å ³)	2081.8 (6)	1259.51 (17)	685.40 (7)	1292.05 (19)
<i>Z</i>	8	4	2	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ^{−1})	0.12	0.10	0.10	0.11
Crystal size (mm)	0.16 × 0.14 × 0.11	0.17 × 0.14 × 0.13	0.16 × 0.15 × 0.12	0.14 × 0.13 × 0.11
Data collection				
Diffractometer	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2008a)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2008a)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2008a)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2008a)
<i>T</i> _{min} , <i>T</i> _{max}	0.931, 0.987	0.960, 0.987	0.955, 0.988	0.929, 0.988
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	31526, 2218, 1304	21653, 2704, 1624	12818, 2526, 1777	20456, 2521, 1722
<i>R</i> _{int}	0.063	0.046	0.030	0.053
(sin θ /λ) _{max} (Å ^{−1})	0.634	0.635	0.605	0.618
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.045, 0.122, 1.03	0.042, 0.129, 1.04	0.044, 0.128, 1.05	0.046, 0.108, 1.05
No. of reflections	2218	2704	2526	2521
No. of parameters	161	175	196	210
No. of restraints	0	0	7	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ^{−3})	0.19, −0.16	0.19, −0.18	0.24, −0.24	0.20, −0.21

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008b), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

pairs of molecules are linked by O—H...O hydrogen bonds to form centrosymmetric *R*₂²(8) dimers. For the simpler analogue 3-phenyl-1*H*-pyrazole-5-carboxylic acid, the structure was described (Zhang *et al.*, 2007) as consisting of chains built from O—H...O and N—H...N hydrogen bonds, which were then linked into sheets by C—H...O hydrogen bonds. However, scrutiny of the atomic coordinates shows that the structure contains no C—H...O hydrogen bonds, and that the combination of one O—H...O hydrogen bond and one N—H...N hydrogen bond generates sheets lying parallel to (100) and containing alternating *R*₂²(8) and *R*₆⁶(28) rings (Fig. 11).

Finally, we note that structures have been reported for each of the precursor sydnones employed here (Fig. 5), for *X* = H (Hope, 1978), *X* = Me (Wang *et al.*, 1984) and *X* = MeO (Fun *et al.*, 2010) although, when *X* = H, there are no atomic coordinates deposited in the Cambridge Structural Database (Groom *et al.*, 2016).

5. Synthesis and crystallization

The precursor sydnones (*A*) (Fig. 5) were prepared from the corresponding anilines (Greco *et al.*, 1962; Wang *et al.*, 1984; Fun *et al.*, 2010). For the synthesis of the esters (II) and (III), a

mixture of the sydnone of type (*A*) having *X* = H for (II) or *X* = CH₃ for (III), (1 mmol) and dimethyl acetylenedicarboxylate (1 mmol) in dry *p*-xylene (10 ml) was heated under reflux for 1 h. The mixtures were then cooled to ambient temperature, the solvent was removed under reduced pressure and the resulting solid products were recrystallized from ethanol. (II): yield 95%, m.p. 373 K. IR (ATR, cm^{−1}) 1712 (C=O), 1582 (C=N). NMR (CDCl₃) δ(¹H) 3.81 (*s*, 3H, O—CH₃), 4.08 (*s*, 3H, O—CH₃), 7.31 (*m*, 1H, H14), 7.40 (*d*, *J* = 7.5 Hz, 2H, H13 & H15), 7.81 (*d*, *J* = 7.5 Hz, 2H, H12 & H16), 9.28 (*s*, 1H, H5). Analysis found C 60.2, H 4.7, N 10.8%, C₁₃H₁₂N₂O₄ requires C 60.0, H 4.6, N 10.8%. (III): yield 93%, m.p. 371 K. IR (ATR, cm^{−1}) 1732 (C=O), 1532 (C=N). NMR (CDCl₃) δ(¹H) 2.21 (*s*, 3H, C—CH₃), 3.82 (*s*, 3H, O—CH₃), 4.10 (*s*, 3H, O—CH₃), 7.48 (*d*, *J* = 7.6 Hz, 2H, H13 & H15), 7.88 (*d*, *J* = 7.6 Hz, 2H, H12 & H16), 8.94 (*s*, 1H, H5). Analysis found C 61.4, H 5.2, N 10.4%, C₁₄H₁₄N₂O₄ requires C 61.3, H 5.1, N 10.2%.

For the synthesis of the acid (I), the ester (II) (1 mmol) and solid sodium hydroxide (2 mmol) were dissolved in a water–ethanol mixture (water:ethanol 80:20 *v/v*, 50 ml). This mixture was heated under reflux for 2h, cooled to ambient temperature and then acidified to pH 2 using dilute aqueous hydrochloric acid. The resulting solid product was collected by filtration,

washed with water and then recrystallized from ethanol. (I): yield 71%, m.p. 508–509 K. IR (ATR, cm^{-1}) 3427 (O—H), 1717 (C=O), 1542 (C=N). NMR (CDCl_3) $\delta(^1\text{H})$ 7.41 (*m*, 1H, H14), 7.53 (*d*, $J = 7.6$ Hz, 2H, H13 & H15), 7.93 (*d*, $J = 7.6$ Hz, 2H, H12 & H16), 7.10 (*s*, 1H, H5). LC-MS m/z 230.9. Analysis found C 57.1, H 3.6, N 12.2%, $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4$ requires C 56.9, H 3.5, N 12.1%. For the synthesis of the hydrazide (IV), the intermediate ester (B) (Fig. 5) was prepared in exactly the same fashion of the esters (II) and (III), yield 90%, m.p. 458 K. A mixture of ester (B) (1 mmol) and hydrazine hydrate (99% aqueous solution, 10 mmol) in ethanol (10 ml) was heated under reflux for 2 h. The mixture was cooled to ambient temperature and the resulting solid product was collected by filtration and then recrystallized from ethanol. (IV): yield 75%, m.p. 502 K. IR (ATR, cm^{-1}) 3354 (N—H), 3308 (N—H), 1650 (C=O), 1562 (C=N). NMR ($\text{DMSO}-d_6$) $\delta(^1\text{H})$ 3.67 (*br*, 6H, N—H), 3.82 (*s*, 3H, O—CH₃), 6.98 (*d*, $J = 7.7$ Hz, 2H, H13 & H15), 7.69 (*d*, $J = 7.7$ Hz, 2H, H12 & H16), 8.91 (*s*, 1H, H5). LC-MS m/z 290.3. Analysis found C 49.5, H 4.8, N 28.8%, $\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}_3$ requires C 49.6, H 4.9, N 29.0%. Crystals of compounds (I)–(IV) suitable for single-crystal X-ray diffraction were selected directly from the purified samples.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. One low-angle reflection, (001) in compound (III), which had been attenuated by the beam stop was removed from the data set. All H atoms were located in difference maps. The H atoms bonded to C atoms were subsequently treated as riding atoms in geometrically idealized position with C—H distances 0.93 Å (aryl and pyrazole) or 0.96 Å (CH₃) and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. For the H atoms bonded to O or N atoms, the atomic coordinates were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ or $1.2U_{\text{eq}}(\text{N})$, leading to the O—H and N—H distances shown in Table 2. It was apparent that one of the ester substituents in compound (III) was disordered over two sets of atomic sites. For the minor disorder component, the bonded distances and the 1,2 non-bonded distances were restrained to be the same as the corresponding distances in the major disorder component, subject to s.u. values of 0.005 and 0.01 Å, respectively. In addition, the anisotropic displacement parameters for the corresponding pairs of atoms in the two disorder components were constrained to be the same, and the two disordered carboxylate fragments were constrained to be planar. Subject to these conditions, the occupancies of the two sets of sites refined to 0.71 (2) and 0.29 (2).

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Four 1-aryl-1*H*-pyrazole-3,4-dicarboxylate derivatives: synthesis, molecular conformation and hydrogen bonding

Asma, Balakrishna Kalluraya, Hemmige S. Yathirajan, Ravindranath S. Rathore and Christopher Glidewell

Computing details

For all structures, data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2/SAINT* (Bruker, 2004); data reduction: *SAINT/XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

1-Phenyl-1*H*-pyrazole-3,4-dicarboxylic acid (I)

Crystal data

$C_{11}H_8N_2O_4$

$M_r = 232.19$

Orthorhombic, *Pbca*

$a = 13.164$ (2) Å

$b = 7.4692$ (9) Å

$c = 21.173$ (3) Å

$V = 2081.8$ (6) Å³

$Z = 8$

$F(000) = 960$

$D_x = 1.482$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2218 reflections

$\theta = 2.5$ – 26.8°

$\mu = 0.12$ mm⁻¹

$T = 296$ K

Block, colourless

$0.16 \times 0.14 \times 0.11$ mm

Data collection

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2008a)

$T_{\min} = 0.931$, $T_{\max} = 0.987$

31526 measured reflections

2218 independent reflections

1304 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 26.8^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -16 \rightarrow 16$

$k = -9 \rightarrow 9$

$l = -26 \rightarrow 26$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.122$

$S = 1.03$

2218 reflections

161 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.9866P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.19$ e Å⁻³

$\Delta\rho_{\min} = -0.16$ e Å⁻³

Extinction correction: SHELXL2014
 (Sheldrick, 2015),
 $F_c^* = k F_c [1 + 0.001 x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0015 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.37444 (14)	0.5732 (2)	0.38946 (7)	0.0382 (4)
N2	0.37411 (13)	0.4662 (2)	0.44062 (7)	0.0361 (4)
C3	0.37378 (16)	0.5767 (2)	0.48951 (9)	0.0318 (4)
C4	0.37462 (16)	0.7576 (2)	0.46953 (10)	0.0341 (5)
C5	0.37519 (17)	0.7475 (3)	0.40517 (10)	0.0416 (5)
H5	0.3760	0.8437	0.3773	0.050*
C11	0.37392 (17)	0.4958 (3)	0.32759 (9)	0.0415 (5)
C12	0.3296 (2)	0.5877 (4)	0.27889 (11)	0.0572 (7)
H12	0.2988	0.6978	0.2863	0.069*
C13	0.3311 (2)	0.5164 (4)	0.21895 (11)	0.0691 (8)
H13	0.3017	0.5787	0.1856	0.083*
C14	0.3756 (2)	0.3540 (5)	0.20857 (13)	0.0718 (9)
H14	0.3771	0.3063	0.1680	0.086*
C15	0.4181 (2)	0.2612 (4)	0.25766 (13)	0.0665 (8)
H15	0.4474	0.1499	0.2503	0.080*
C16	0.41776 (19)	0.3311 (3)	0.31810 (12)	0.0548 (7)
H16	0.4465	0.2682	0.3515	0.066*
C31	0.37166 (17)	0.4926 (3)	0.55265 (9)	0.0377 (5)
O31	0.37408 (14)	0.33081 (19)	0.55896 (7)	0.0540 (5)
O32	0.36707 (14)	0.5958 (2)	0.60230 (7)	0.0524 (5)
H32	0.3671 (19)	0.724 (4)	0.5880 (13)	0.079*
C41	0.37522 (17)	0.9202 (3)	0.50785 (11)	0.0412 (5)
O41	0.37173 (14)	0.91999 (19)	0.56526 (8)	0.0578 (5)
O42	0.37916 (14)	1.06752 (19)	0.47441 (8)	0.0528 (5)
H42	0.375 (2)	1.164 (4)	0.4979 (13)	0.079*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0500 (11)	0.0337 (9)	0.0309 (9)	0.0033 (9)	−0.0029 (8)	−0.0027 (7)
N2	0.0487 (11)	0.0296 (9)	0.0301 (9)	0.0015 (8)	−0.0021 (9)	−0.0017 (7)
C3	0.0375 (11)	0.0287 (9)	0.0293 (10)	0.0002 (9)	−0.0010 (9)	−0.0059 (8)
C4	0.0404 (12)	0.0279 (10)	0.0340 (12)	0.0011 (10)	0.0015 (11)	−0.0031 (8)
C5	0.0562 (14)	0.0302 (11)	0.0383 (12)	0.0037 (10)	−0.0012 (12)	0.0011 (9)
C11	0.0487 (14)	0.0483 (12)	0.0276 (11)	−0.0013 (12)	−0.0019 (10)	−0.0099 (10)

C12	0.0711 (18)	0.0649 (16)	0.0356 (13)	0.0016 (14)	−0.0049 (12)	−0.0026 (12)
C13	0.083 (2)	0.092 (2)	0.0323 (14)	−0.0064 (18)	−0.0068 (13)	−0.0047 (14)
C14	0.074 (2)	0.107 (2)	0.0348 (14)	−0.0165 (19)	0.0040 (15)	−0.0250 (15)
C15	0.0658 (18)	0.0745 (18)	0.0591 (18)	0.0048 (16)	0.0012 (15)	−0.0330 (15)
C16	0.0606 (16)	0.0594 (16)	0.0445 (14)	0.0108 (13)	−0.0067 (13)	−0.0193 (12)
C31	0.0493 (13)	0.0329 (11)	0.0309 (11)	−0.0019 (10)	0.0021 (11)	−0.0031 (9)
O31	0.0923 (13)	0.0305 (8)	0.0392 (9)	0.0023 (9)	0.0035 (9)	0.0028 (7)
O32	0.0871 (13)	0.0404 (9)	0.0296 (8)	−0.0052 (9)	0.0042 (8)	−0.0071 (7)
C41	0.0431 (13)	0.0297 (11)	0.0507 (14)	−0.0011 (10)	0.0061 (11)	−0.0054 (10)
O41	0.0945 (14)	0.0358 (9)	0.0432 (10)	−0.0070 (9)	0.0135 (9)	−0.0126 (7)
O42	0.0783 (13)	0.0255 (8)	0.0547 (11)	0.0011 (8)	0.0056 (9)	−0.0049 (7)

Geometric parameters (Å, °)

N1—C5	1.344 (2)	C13—C14	1.365 (4)
N1—N2	1.346 (2)	C13—H13	0.9300
N1—C11	1.432 (2)	C14—C15	1.369 (4)
N2—C3	1.324 (2)	C14—H14	0.9300
C3—C4	1.416 (3)	C15—C16	1.382 (3)
C3—C31	1.477 (3)	C15—H15	0.9300
C4—C5	1.365 (3)	C16—H16	0.9300
C4—C41	1.461 (3)	C31—O31	1.216 (2)
C5—H5	0.9300	C31—O32	1.305 (2)
C11—C12	1.369 (3)	O32—H32	1.00 (3)
C11—C16	1.374 (3)	C41—O41	1.216 (3)
C12—C13	1.377 (3)	C41—O42	1.309 (2)
C12—H12	0.9300	O42—H42	0.88 (3)
C5—N1—N2	112.07 (16)	C14—C13—H13	120.1
C5—N1—C11	128.16 (18)	C12—C13—H13	120.1
N2—N1—C11	119.77 (17)	C13—C14—C15	120.2 (2)
C3—N2—N1	105.03 (15)	C13—C14—H14	119.9
N2—C3—C4	111.17 (17)	C15—C14—H14	119.9
N2—C3—C31	116.28 (16)	C14—C15—C16	120.7 (3)
C4—C3—C31	132.55 (17)	C14—C15—H15	119.7
C5—C4—C3	104.21 (16)	C16—C15—H15	119.7
C5—C4—C41	126.91 (18)	C11—C16—C15	118.4 (2)
C3—C4—C41	128.87 (19)	C11—C16—H16	120.8
N1—C5—C4	107.50 (18)	C15—C16—H16	120.8
N1—C5—H5	126.2	O31—C31—O32	119.95 (19)
C4—C5—H5	126.2	O31—C31—C3	121.43 (18)
C12—C11—C16	121.2 (2)	O32—C31—C3	118.62 (17)
C12—C11—N1	119.2 (2)	C31—O32—H32	108.6 (15)
C16—C11—N1	119.6 (2)	O41—C41—O42	122.89 (19)
C11—C12—C13	119.6 (3)	O41—C41—C4	123.62 (19)
C11—C12—H12	120.2	O42—C41—C4	113.48 (19)
C13—C12—H12	120.2	C41—O42—H42	112.5 (18)
C14—C13—C12	119.9 (3)		

C5—N1—N2—C3	0.5 (2)	C16—C11—C12—C13	−1.6 (4)
C11—N1—N2—C3	−179.43 (19)	N1—C11—C12—C13	178.4 (2)
N1—N2—C3—C4	−0.4 (2)	C11—C12—C13—C14	0.6 (4)
N1—N2—C3—C31	179.03 (18)	C12—C13—C14—C15	0.6 (4)
N2—C3—C4—C5	0.2 (3)	C13—C14—C15—C16	−0.9 (4)
C31—C3—C4—C5	−179.2 (2)	C12—C11—C16—C15	1.3 (4)
N2—C3—C4—C41	−179.6 (2)	N1—C11—C16—C15	−178.7 (2)
C31—C3—C4—C41	1.1 (4)	C14—C15—C16—C11	−0.1 (4)
N2—N1—C5—C4	−0.4 (3)	N2—C3—C31—O31	2.7 (3)
C11—N1—C5—C4	179.5 (2)	C4—C3—C31—O31	−178.0 (2)
C3—C4—C5—N1	0.2 (3)	N2—C3—C31—O32	−177.2 (2)
C41—C4—C5—N1	179.9 (2)	C4—C3—C31—O32	2.1 (4)
C5—N1—C11—C12	−29.3 (4)	C5—C4—C41—O41	177.8 (2)
N2—N1—C11—C12	150.6 (2)	C3—C4—C41—O41	−2.5 (4)
C5—N1—C11—C16	150.6 (2)	C5—C4—C41—O42	−1.7 (3)
N2—N1—C11—C16	−29.4 (3)	C3—C4—C41—O42	178.0 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O32—H32 \cdots O41	1.00 (3)	1.54 (3)	2.546 (2)	178 (2)
O42—H42 \cdots O31 ⁱ	0.88 (3)	1.80 (3)	2.660 (2)	168 (3)
O42—H42 \cdots N2 ⁱ	0.88 (3)	2.56 (3)	3.063 (2)	117 (2)
C14—H14 \cdots O31 ⁱⁱ	0.93	2.53	3.456 (3)	177
C12—H12 \cdots Cg1 ⁱⁱⁱ	0.93	2.86	3.685 (3)	148
C15—H15 \cdots Cg1 ^{iv}	0.93	2.92	3.755 (3)	151

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *−y*+1/2, *z*−1/2; (iii) *−x*+1/2, *y*+1/2, *z*; (iv) *−x*+1, *y*+1/2, *−z*+1/2.

Dimethyl 1-phenyl-1*H*-pyrazole-3,4-dicarboxylate (II)

Crystal data

C₁₃H₁₂N₂O₄
M_r = 260.25
 Monoclinic, *P*2₁/*n*
a = 5.9000 (4) Å
b = 14.5273 (12) Å
c = 14.8726 (12) Å
 β = 98.867 (3)°
V = 1259.51 (17) Å³
Z = 4

F(000) = 544
D_x = 1.372 Mg m^{−3}
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 2704 reflections
 θ = 2.8–26.8°
 μ = 0.10 mm^{−1}
T = 296 K
 Block, orange
 0.17 × 0.14 × 0.13 mm

Data collection

Bruker Kappa APEXII CCD
 diffractometer
 Radiation source: fine focus sealed tube
 Graphite monochromator
 φ and ω scans

Absorption correction: multi-scan
 (SADABS; Sheldrick, 2008a)
T_{min} = 0.960, *T_{max}* = 0.987
 21653 measured reflections
 2704 independent reflections
 1624 reflections with *I* > 2 σ (*I*)

$R_{\text{int}} = 0.046$
 $\theta_{\text{max}} = 26.8^\circ$, $\theta_{\text{min}} = 2.8^\circ$
 $h = -6 \rightarrow 7$

$k = -18 \rightarrow 18$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.129$
 $S = 1.04$
 2704 reflections
 175 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.3996P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2014
 (Sheldrick, 2015),
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.014 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.5660 (3)	0.34915 (11)	0.69867 (11)	0.0412 (4)
N2	0.4302 (3)	0.27659 (11)	0.71300 (11)	0.0437 (4)
C3	0.2695 (3)	0.27445 (13)	0.64031 (13)	0.0410 (5)
C4	0.3003 (3)	0.34570 (14)	0.57864 (13)	0.0416 (5)
C5	0.4919 (3)	0.39140 (14)	0.61917 (13)	0.0438 (5)
H5	0.5587	0.4424	0.5959	0.053*
C11	0.7563 (3)	0.37397 (13)	0.76566 (13)	0.0414 (5)
C12	0.9342 (3)	0.42372 (15)	0.73977 (15)	0.0490 (5)
H12	0.9325	0.4396	0.6791	0.059*
C13	1.1146 (4)	0.44954 (17)	0.80489 (17)	0.0617 (6)
H13	1.2344	0.4838	0.7880	0.074*
C14	1.1201 (4)	0.42556 (18)	0.89396 (18)	0.0683 (7)
H14	1.2442	0.4423	0.9373	0.082*
C15	0.9413 (4)	0.3766 (2)	0.91897 (17)	0.0738 (8)
H15	0.9443	0.3608	0.9797	0.089*
C16	0.7567 (4)	0.35049 (16)	0.85540 (15)	0.0588 (6)
H16	0.6353	0.3177	0.8728	0.071*
C31	0.0986 (4)	0.19862 (14)	0.62958 (15)	0.0461 (5)
O31	0.0528 (3)	0.15354 (14)	0.56252 (12)	0.0900 (7)
O32	0.0058 (3)	0.18661 (10)	0.70371 (10)	0.0596 (4)
C32	-0.1630 (4)	0.11423 (17)	0.70126 (19)	0.0701 (7)
H32A	-0.2925	0.1283	0.6559	0.105*
H32B	-0.2120	0.1094	0.7597	0.105*
H32C	-0.0966	0.0569	0.6866	0.105*
C41	0.1559 (3)	0.37509 (14)	0.49430 (14)	0.0453 (5)

O41	0.2172 (3)	0.42800 (13)	0.44075 (11)	0.0740 (5)
O42	−0.0501 (2)	0.33820 (12)	0.48518 (10)	0.0614 (5)
C42	−0.2056 (4)	0.3587 (2)	0.40269 (17)	0.0704 (7)
H42A	−0.2395	0.4233	0.4004	0.106*
H42B	−0.3449	0.3244	0.4020	0.106*
H42C	−0.1355	0.3419	0.3509	0.106*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0431 (9)	0.0388 (9)	0.0406 (10)	−0.0017 (7)	0.0024 (7)	0.0039 (7)
N2	0.0470 (9)	0.0380 (9)	0.0449 (10)	−0.0039 (7)	0.0027 (8)	0.0052 (7)
C3	0.0437 (11)	0.0410 (11)	0.0379 (11)	−0.0009 (9)	0.0049 (9)	−0.0003 (9)
C4	0.0433 (11)	0.0430 (11)	0.0382 (11)	0.0000 (9)	0.0055 (9)	0.0021 (9)
C5	0.0456 (11)	0.0450 (11)	0.0407 (11)	−0.0029 (9)	0.0065 (9)	0.0057 (9)
C11	0.0408 (10)	0.0389 (11)	0.0425 (12)	0.0041 (9)	−0.0002 (9)	−0.0004 (9)
C12	0.0407 (11)	0.0571 (13)	0.0493 (12)	0.0034 (10)	0.0069 (10)	−0.0016 (10)
C13	0.0429 (12)	0.0712 (16)	0.0695 (17)	−0.0039 (11)	0.0043 (12)	−0.0028 (13)
C14	0.0550 (14)	0.0788 (18)	0.0641 (17)	−0.0031 (13)	−0.0130 (12)	−0.0067 (14)
C15	0.0765 (17)	0.091 (2)	0.0477 (15)	−0.0081 (15)	−0.0110 (13)	0.0077 (13)
C16	0.0609 (14)	0.0625 (15)	0.0500 (14)	−0.0100 (11)	−0.0010 (11)	0.0084 (11)
C31	0.0522 (12)	0.0398 (11)	0.0445 (12)	−0.0027 (9)	0.0018 (10)	−0.0008 (9)
O31	0.1229 (16)	0.0839 (13)	0.0665 (12)	−0.0478 (12)	0.0247 (11)	−0.0260 (10)
O32	0.0649 (10)	0.0556 (9)	0.0613 (10)	−0.0205 (8)	0.0191 (8)	−0.0043 (8)
C32	0.0586 (14)	0.0551 (15)	0.100 (2)	−0.0169 (11)	0.0222 (14)	0.0029 (14)
C41	0.0473 (11)	0.0485 (12)	0.0398 (11)	−0.0036 (10)	0.0057 (9)	0.0000 (9)
O41	0.0718 (11)	0.0869 (13)	0.0584 (10)	−0.0226 (9)	−0.0054 (8)	0.0310 (9)
O42	0.0476 (9)	0.0812 (11)	0.0519 (10)	−0.0100 (8)	−0.0034 (7)	0.0123 (8)
C42	0.0536 (14)	0.0910 (19)	0.0593 (16)	0.0017 (13)	−0.0144 (12)	0.0035 (13)

Geometric parameters (Å, °)

N1—C5	1.344 (2)	C14—H14	0.9300
N1—N2	1.360 (2)	C15—C16	1.381 (3)
N1—C11	1.428 (2)	C15—H15	0.9300
N2—C3	1.324 (2)	C16—H16	0.9300
C3—C4	1.413 (3)	C31—O31	1.189 (2)
C3—C31	1.485 (3)	C31—O32	1.316 (2)
C4—C5	1.368 (3)	O32—C32	1.445 (3)
C4—C41	1.467 (3)	C32—H32A	0.9600
C5—H5	0.9300	C32—H32B	0.9600
C11—C16	1.377 (3)	C32—H32C	0.9600
C11—C12	1.377 (3)	C41—O41	1.202 (2)
C12—C13	1.376 (3)	C41—O42	1.316 (2)
C12—H12	0.9300	O42—C42	1.445 (3)
C13—C14	1.365 (3)	C42—H42A	0.9600
C13—H13	0.9300	C42—H42B	0.9600
C14—C15	1.370 (4)	C42—H42C	0.9600

C5—N1—N2	111.86 (15)	C14—C15—H15	119.5
C5—N1—C11	127.77 (16)	C16—C15—H15	119.5
N2—N1—C11	120.34 (15)	C11—C16—C15	118.6 (2)
C3—N2—N1	104.78 (15)	C11—C16—H16	120.7
N2—C3—C4	111.42 (17)	C15—C16—H16	120.7
N2—C3—C31	119.60 (17)	O31—C31—O32	124.04 (19)
C4—C3—C31	128.80 (18)	O31—C31—C3	124.1 (2)
C5—C4—C3	104.46 (17)	O32—C31—C3	111.82 (17)
C5—C4—C41	124.54 (18)	C31—O32—C32	116.71 (18)
C3—C4—C41	130.71 (18)	O32—C32—H32A	109.5
N1—C5—C4	107.48 (17)	O32—C32—H32B	109.5
N1—C5—H5	126.3	H32A—C32—H32B	109.5
C4—C5—H5	126.3	O32—C32—H32C	109.5
C16—C11—C12	120.88 (19)	H32A—C32—H32C	109.5
C16—C11—N1	119.82 (18)	H32B—C32—H32C	109.5
C12—C11—N1	119.27 (18)	O41—C41—O42	124.03 (19)
C13—C12—C11	119.1 (2)	O41—C41—C4	123.92 (19)
C13—C12—H12	120.5	O42—C41—C4	112.03 (17)
C11—C12—H12	120.5	C41—O42—C42	117.33 (18)
C14—C13—C12	120.9 (2)	O42—C42—H42A	109.5
C14—C13—H13	119.5	O42—C42—H42B	109.5
C12—C13—H13	119.5	H42A—C42—H42B	109.5
C13—C14—C15	119.4 (2)	O42—C42—H42C	109.5
C13—C14—H14	120.3	H42A—C42—H42C	109.5
C15—C14—H14	120.3	H42B—C42—H42C	109.5
C14—C15—C16	121.0 (2)		
C5—N1—N2—C3	0.1 (2)	C11—C12—C13—C14	0.8 (3)
C11—N1—N2—C3	178.19 (16)	C12—C13—C14—C15	−1.3 (4)
N1—N2—C3—C4	−0.1 (2)	C13—C14—C15—C16	0.6 (4)
N1—N2—C3—C31	175.56 (16)	C12—C11—C16—C15	−1.0 (3)
N2—C3—C4—C5	0.0 (2)	N1—C11—C16—C15	−179.0 (2)
C31—C3—C4—C5	−175.11 (19)	C14—C15—C16—C11	0.5 (4)
N2—C3—C4—C41	−173.87 (19)	N2—C3—C31—O31	−130.0 (2)
C31—C3—C4—C41	11.0 (3)	C4—C3—C31—O31	44.8 (3)
N2—N1—C5—C4	−0.1 (2)	N2—C3—C31—O32	49.3 (2)
C11—N1—C5—C4	−177.99 (17)	C4—C3—C31—O32	−135.9 (2)
C3—C4—C5—N1	0.0 (2)	O31—C31—O32—C32	−0.6 (3)
C41—C4—C5—N1	174.43 (18)	C3—C31—O32—C32	−179.80 (17)
C5—N1—C11—C16	153.3 (2)	C5—C4—C41—O41	18.7 (3)
N2—N1—C11—C16	−24.4 (3)	C3—C4—C41—O41	−168.5 (2)
C5—N1—C11—C12	−24.7 (3)	C5—C4—C41—O42	−160.01 (19)
N2—N1—C11—C12	157.57 (17)	C3—C4—C41—O42	12.8 (3)
C16—C11—C12—C13	0.3 (3)	O41—C41—O42—C42	4.0 (3)
N1—C11—C12—C13	178.35 (18)	C4—C41—O42—C42	−177.34 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C5—H5 \cdots O41 ⁱ	0.93	2.41	3.331 (3)	170

Symmetry code: (i) $-x+1, -y+1, -z+1$.**Dimethyl 1-(4-methylphenyl)-1*H*-pyrazole-3,4-dicarboxylate (III)***Crystal data*

$C_{14}H_{14}N_2O_4$	$Z = 2$
$M_r = 274.27$	$F(000) = 288$
Triclinic, $P\bar{1}$	$D_x = 1.329 \text{ Mg m}^{-3}$
$a = 7.6546 (5) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 8.0959 (5) \text{ \AA}$	Cell parameters from 2526 reflections
$c = 11.3065 (6) \text{ \AA}$	$\theta = 2.6\text{--}25.5^\circ$
$\alpha = 78.988 (3)^\circ$	$\mu = 0.10 \text{ mm}^{-1}$
$\beta = 85.527 (3)^\circ$	$T = 296 \text{ K}$
$\gamma = 87.548 (4)^\circ$	Block, brown
$V = 685.40 (7) \text{ \AA}^3$	$0.16 \times 0.15 \times 0.12 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD diffractometer	12818 measured reflections
Radiation source: fine focus sealed tube	2526 independent reflections
Graphite monochromator	1777 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.030$
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	$\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 2.6^\circ$
$T_{\text{min}} = 0.955$, $T_{\text{max}} = 0.988$	$h = -9 \rightarrow 9$
	$k = -9 \rightarrow 9$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 0.2439P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
2526 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$
196 parameters	Extinction correction: SHELXL2014
7 restraints	(Sheldrick, 2015),
Hydrogen site location: inferred from neighbouring sites	$F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.024 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.3938 (2)	0.7228 (2)	0.38159 (13)	0.0446 (4)	
N2	0.4458 (2)	0.7773 (2)	0.26297 (14)	0.0477 (4)	

C3	0.3163 (2)	0.7413 (3)	0.20267 (16)	0.0426 (5)	
C4	0.1791 (2)	0.6623 (2)	0.28127 (16)	0.0428 (5)	
C5	0.2362 (3)	0.6525 (3)	0.39480 (17)	0.0464 (5)	
H5	0.1765	0.6057	0.4675	0.056*	
C11	0.5036 (3)	0.7482 (3)	0.47287 (17)	0.0446 (5)	
C12	0.4529 (3)	0.6979 (3)	0.59269 (19)	0.0634 (7)	
H12	0.3468	0.6450	0.6157	0.076*	
C13	0.5596 (3)	0.7261 (3)	0.6790 (2)	0.0663 (7)	
H13	0.5240	0.6911	0.7602	0.080*	
C14	0.7168 (3)	0.8041 (3)	0.6491 (2)	0.0567 (6)	
C15	0.7647 (3)	0.8500 (4)	0.5289 (2)	0.0758 (8)	
H15	0.8717	0.9011	0.5059	0.091*	
C16	0.6612 (3)	0.8238 (3)	0.4403 (2)	0.0686 (7)	
H16	0.6979	0.8572	0.3592	0.082*	
C14I	0.8328 (4)	0.8354 (3)	0.7436 (2)	0.0797 (8)	
H14A	0.7677	0.8190	0.8208	0.119*	
H14B	0.8726	0.9489	0.7233	0.119*	
H14C	0.9319	0.7584	0.7470	0.119*	
C31A	0.3342 (3)	0.7907 (3)	0.06874 (18)	0.0505 (5)	0.71 (2)
O31A	0.4587 (11)	0.7554 (17)	0.0048 (5)	0.093 (3)	0.71 (2)
O32A	0.2044 (10)	0.8936 (9)	0.0288 (6)	0.0542 (14)	0.71 (2)
C32A	0.2113 (19)	0.9575 (17)	−0.0998 (7)	0.0653 (16)	0.71 (2)
H32A	0.2195	0.8650	−0.1421	0.098*	0.71 (2)
H32B	0.3121	1.0261	−0.1233	0.098*	0.71 (2)
H32C	0.1070	1.0239	−0.1196	0.098*	0.71 (2)
C31B	0.3342 (3)	0.7907 (3)	0.06874 (18)	0.0505 (5)	0.29 (2)
O31B	0.413 (2)	0.6979 (19)	0.0113 (14)	0.093 (3)	0.29 (2)
O32B	0.233 (2)	0.9199 (19)	0.0250 (15)	0.0542 (14)	0.29 (2)
C32B	0.234 (5)	0.966 (4)	−0.1050 (17)	0.0653 (16)	0.29 (2)
H32D	0.1476	0.9035	−0.1334	0.098*	0.29 (2)
H32E	0.3479	0.9404	−0.1404	0.098*	0.29 (2)
H32F	0.2080	1.0842	−0.1275	0.098*	0.29 (2)
C41	0.0150 (3)	0.5929 (3)	0.25809 (17)	0.0456 (5)	
O41	−0.0860 (2)	0.5221 (2)	0.33564 (14)	0.0756 (6)	
O42	−0.01086 (18)	0.61505 (19)	0.14123 (12)	0.0550 (4)	
C42	−0.1738 (3)	0.5551 (3)	0.1112 (2)	0.0679 (7)	
H42A	−0.2701	0.6035	0.1538	0.102*	
H42B	−0.1748	0.4346	0.1339	0.102*	
H42C	−0.1847	0.5873	0.0258	0.102*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0440 (9)	0.0561 (11)	0.0331 (8)	−0.0093 (8)	−0.0050 (7)	−0.0041 (7)
N2	0.0458 (10)	0.0613 (11)	0.0345 (9)	−0.0105 (8)	−0.0028 (7)	−0.0030 (8)
C3	0.0397 (11)	0.0511 (12)	0.0369 (10)	−0.0032 (9)	−0.0047 (8)	−0.0067 (9)
C4	0.0407 (10)	0.0505 (12)	0.0372 (10)	−0.0050 (9)	−0.0045 (8)	−0.0063 (9)
C5	0.0436 (11)	0.0567 (13)	0.0373 (10)	−0.0110 (10)	−0.0009 (8)	−0.0036 (9)

C11	0.0449 (11)	0.0505 (12)	0.0390 (11)	−0.0044 (9)	−0.0084 (8)	−0.0073 (9)
C12	0.0539 (13)	0.0937 (19)	0.0424 (12)	−0.0174 (12)	−0.0051 (10)	−0.0085 (12)
C13	0.0673 (16)	0.0924 (19)	0.0403 (12)	−0.0055 (14)	−0.0108 (11)	−0.0117 (12)
C14	0.0644 (15)	0.0543 (13)	0.0555 (14)	0.0014 (11)	−0.0219 (11)	−0.0142 (10)
C15	0.0671 (16)	0.097 (2)	0.0649 (16)	−0.0367 (14)	−0.0163 (12)	−0.0063 (14)
C16	0.0661 (15)	0.0951 (19)	0.0441 (12)	−0.0334 (14)	−0.0082 (11)	−0.0035 (12)
C141	0.092 (2)	0.0787 (19)	0.0782 (18)	0.0009 (15)	−0.0441 (15)	−0.0260 (14)
C31A	0.0409 (11)	0.0727 (15)	0.0380 (11)	−0.0064 (11)	−0.0031 (9)	−0.0093 (10)
O31A	0.070 (3)	0.159 (6)	0.0434 (12)	0.035 (4)	0.0031 (17)	−0.010 (2)
O32A	0.054 (2)	0.062 (2)	0.0395 (9)	−0.008 (2)	0.0009 (13)	0.0060 (12)
C32A	0.075 (4)	0.0739 (19)	0.0406 (14)	−0.017 (3)	−0.0089 (17)	0.0103 (13)
C31B	0.0409 (11)	0.0727 (15)	0.0380 (11)	−0.0064 (11)	−0.0031 (9)	−0.0093 (10)
O31B	0.070 (3)	0.159 (6)	0.0434 (12)	0.035 (4)	0.0031 (17)	−0.010 (2)
O32B	0.054 (2)	0.062 (2)	0.0395 (9)	−0.008 (2)	0.0009 (13)	0.0060 (12)
C32B	0.075 (4)	0.0739 (19)	0.0406 (14)	−0.017 (3)	−0.0089 (17)	0.0103 (13)
C41	0.0421 (11)	0.0557 (13)	0.0387 (11)	−0.0047 (10)	−0.0025 (9)	−0.0077 (9)
O41	0.0581 (10)	0.1211 (15)	0.0449 (9)	−0.0394 (10)	0.0017 (7)	−0.0031 (9)
O42	0.0519 (9)	0.0729 (10)	0.0403 (8)	−0.0177 (7)	−0.0088 (6)	−0.0048 (7)
C42	0.0550 (14)	0.0942 (19)	0.0590 (14)	−0.0187 (13)	−0.0173 (11)	−0.0169 (13)

Geometric parameters (Å, °)

N1—C5	1.341 (2)	C141—H14A	0.9600
N1—N2	1.363 (2)	C141—H14B	0.9600
N1—C11	1.430 (2)	C141—H14C	0.9600
N2—C3	1.319 (2)	C31A—O31A	1.209 (4)
C3—C4	1.413 (3)	C31A—O32A	1.319 (3)
C3—C31A	1.487 (3)	O32A—C32A	1.446 (3)
C4—C5	1.375 (3)	C32A—H32A	0.9600
C4—C41	1.459 (3)	C32A—H32B	0.9600
C5—H5	0.9300	C32A—H32C	0.9600
C11—C12	1.368 (3)	O32B—C32B	1.445 (5)
C11—C16	1.369 (3)	C32B—H32D	0.9600
C12—C13	1.378 (3)	C32B—H32E	0.9600
C12—H12	0.9300	C32B—H32F	0.9600
C13—C14	1.372 (3)	C41—O41	1.198 (2)
C13—H13	0.9300	C41—O42	1.328 (2)
C14—C15	1.363 (3)	O42—C42	1.445 (2)
C14—C141	1.505 (3)	C42—H42A	0.9600
C15—C16	1.377 (3)	C42—H42B	0.9600
C15—H15	0.9300	C42—H42C	0.9600
C16—H16	0.9300		
C5—N1—N2	111.67 (15)	C14—C141—H14B	109.5
C5—N1—C11	128.79 (16)	H14A—C141—H14B	109.5
N2—N1—C11	119.52 (15)	C14—C141—H14C	109.5
C3—N2—N1	105.05 (15)	H14A—C141—H14C	109.5
N2—C3—C4	111.50 (16)	H14B—C141—H14C	109.5

N2—C3—C31A	117.41 (17)	O31A—C31A—O32A	123.5 (3)
C4—C3—C31A	131.07 (17)	O31A—C31A—C3	125.0 (3)
C5—C4—C3	104.27 (16)	O32A—C31A—C3	111.1 (3)
C5—C4—C41	123.78 (17)	C31A—O32A—C32A	116.5 (3)
C3—C4—C41	131.86 (17)	O32A—C32A—H32A	109.5
N1—C5—C4	107.50 (17)	O32A—C32A—H32B	109.5
N1—C5—H5	126.2	H32A—C32A—H32B	109.5
C4—C5—H5	126.2	O32A—C32A—H32C	109.5
C12—C11—C16	119.48 (19)	H32A—C32A—H32C	109.5
C12—C11—N1	120.75 (18)	H32B—C32A—H32C	109.5
C16—C11—N1	119.77 (18)	O32B—C32B—H32D	109.5
C11—C12—C13	119.7 (2)	O32B—C32B—H32E	109.5
C11—C12—H12	120.1	H32D—C32B—H32E	109.5
C13—C12—H12	120.1	O32B—C32B—H32F	109.5
C14—C13—C12	122.1 (2)	H32D—C32B—H32F	109.5
C14—C13—H13	119.0	H32E—C32B—H32F	109.5
C12—C13—H13	119.0	O41—C41—O42	123.08 (18)
C15—C14—C13	116.7 (2)	O41—C41—C4	123.97 (18)
C15—C14—C141	121.4 (2)	O42—C41—C4	112.95 (17)
C13—C14—C141	121.9 (2)	C41—O42—C42	116.23 (16)
C14—C15—C16	122.7 (2)	O42—C42—H42A	109.5
C14—C15—H15	118.6	O42—C42—H42B	109.5
C16—C15—H15	118.6	H42A—C42—H42B	109.5
C11—C16—C15	119.3 (2)	O42—C42—H42C	109.5
C11—C16—H16	120.4	H42A—C42—H42C	109.5
C15—C16—H16	120.4	H42B—C42—H42C	109.5
C14—C141—H14A	109.5		
C5—N1—N2—C3	0.7 (2)	C12—C13—C14—C15	−1.3 (4)
C11—N1—N2—C3	−177.91 (17)	C12—C13—C14—C141	179.7 (2)
N1—N2—C3—C4	−0.2 (2)	C13—C14—C15—C16	1.3 (4)
N1—N2—C3—C31A	178.57 (18)	C141—C14—C15—C16	−179.7 (3)
N2—C3—C4—C5	−0.3 (2)	C12—C11—C16—C15	−0.9 (4)
C31A—C3—C4—C5	−178.9 (2)	N1—C11—C16—C15	179.1 (2)
N2—C3—C4—C41	−176.7 (2)	C14—C15—C16—C11	−0.2 (4)
C31A—C3—C4—C41	4.7 (4)	N2—C3—C31A—O31A	52.4 (9)
N2—N1—C5—C4	−0.9 (2)	C4—C3—C31A—O31A	−129.1 (9)
C11—N1—C5—C4	177.57 (18)	N2—C3—C31A—O32A	−121.0 (5)
C3—C4—C5—N1	0.7 (2)	C4—C3—C31A—O32A	57.5 (6)
C41—C4—C5—N1	177.50 (18)	O31A—C31A—O32A—C32A	3.6 (10)
C5—N1—C11—C12	0.3 (3)	C3—C31A—O32A—C32A	177.1 (8)
N2—N1—C11—C12	178.6 (2)	C5—C4—C41—O41	0.6 (3)
C5—N1—C11—C16	−179.7 (2)	C3—C4—C41—O41	176.5 (2)
N2—N1—C11—C16	−1.4 (3)	C5—C4—C41—O42	−178.86 (19)
C16—C11—C12—C13	0.9 (4)	C3—C4—C41—O42	−3.0 (3)
N1—C11—C12—C13	−179.0 (2)	O41—C41—O42—C42	2.7 (3)
C11—C12—C13—C14	0.2 (4)	C4—C41—O42—C42	−177.82 (18)

Hydrogen-bond geometry (\AA , $^\circ$)

$D\cdots H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots O41^i$	0.93	2.33	3.249 (3)	168
$C12-H12\cdots O41^i$	0.93	2.43	3.352 (3)	173

Symmetry code: (i) $-x, -y+1, -z+1$.**1-(4-Methoxyphenyl)-1*H*-pyrazole-3,4-dicarbohydrazide (IV)***Crystal data* $C_{12}H_{14}N_6O_3$ $M_r = 290.29$ Monoclinic, $P2_1/n$ $a = 7.6030$ (6) \AA $b = 22.6605$ (19) \AA $c = 7.6751$ (7) \AA $\beta = 102.284$ (3) $^\circ$ $V = 1292.05$ (19) \AA^3 $Z = 4$ $F(000) = 608$ $D_x = 1.492$ Mg m^{-3} Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 2521 reflections

 $\theta = 2.9\text{--}26.1^\circ$ $\mu = 0.11$ mm^{-1} $T = 296$ K

Block, colourless

 $0.14 \times 0.13 \times 0.11$ mm*Data collection*

Bruker Kappa APEXII CCD

diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 2008a)

 $T_{\min} = 0.929$, $T_{\max} = 0.988$

20456 measured reflections

2521 independent reflections

1722 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.053$ $\theta_{\max} = 26.1^\circ$, $\theta_{\min} = 2.9^\circ$ $h = -9 \rightarrow 9$ $k = -27 \rightarrow 27$ $l = -9 \rightarrow 9$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.046$ $wR(F^2) = 0.108$ $S = 1.05$

2521 reflections

210 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 1.1086P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.20$ e \AA^{-3} $\Delta\rho_{\min} = -0.21$ e \AA^{-3}

Extinction correction: SHELXL2014

(Sheldrick, 2015),

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0045 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.7660 (2)	0.36969 (8)	0.6437 (2)	0.0283 (4)

N2	0.7948 (2)	0.32224 (8)	0.5473 (2)	0.0314 (5)
C3	0.7018 (3)	0.33229 (9)	0.3822 (3)	0.0275 (5)
C4	0.6115 (3)	0.38765 (9)	0.3717 (3)	0.0280 (5)
C5	0.6564 (3)	0.40941 (10)	0.5433 (3)	0.0298 (5)
H5	0.6181	0.4450	0.5828	0.036*
C11	0.8572 (3)	0.37355 (9)	0.8268 (3)	0.0276 (5)
C12	0.8449 (3)	0.42341 (10)	0.9244 (3)	0.0344 (6)
H12	0.7747	0.4550	0.8727	0.041*
C13	0.9380 (3)	0.42666 (11)	1.1013 (3)	0.0365 (6)
H13	0.9289	0.4603	1.1681	0.044*
C14	1.0436 (3)	0.38002 (10)	1.1778 (3)	0.0317 (5)
C15	1.0555 (3)	0.33004 (10)	1.0777 (3)	0.0368 (6)
H15	1.1270	0.2986	1.1285	0.044*
C16	0.9622 (3)	0.32644 (10)	0.9034 (3)	0.0352 (6)
H16	0.9696	0.2925	0.8372	0.042*
O14	1.1404 (2)	0.37883 (8)	1.3504 (2)	0.0444 (5)
C14I	1.1307 (4)	0.42931 (12)	1.4580 (3)	0.0493 (7)
H14A	1.1762	0.4631	1.4063	0.074*
H14B	1.2016	0.4227	1.5757	0.074*
H14C	1.0077	0.4362	1.4647	0.074*
C31	0.7103 (3)	0.28637 (9)	0.2463 (3)	0.0295 (5)
O31	0.6069 (2)	0.28624 (7)	0.0961 (2)	0.0414 (5)
N31	0.8329 (3)	0.24513 (8)	0.2954 (3)	0.0356 (5)
H31	0.911 (3)	0.2477 (11)	0.397 (3)	0.043*
N32	0.8637 (3)	0.19995 (10)	0.1787 (3)	0.0520 (6)
H32A	0.782 (4)	0.2047 (12)	0.064 (4)	0.062*
H32B	0.841 (4)	0.1612 (13)	0.232 (4)	0.062*
C41	0.5024 (3)	0.42229 (10)	0.2236 (3)	0.0301 (5)
O41	0.4610 (2)	0.47395 (7)	0.2471 (2)	0.0456 (5)
N41	0.4562 (3)	0.39535 (9)	0.0672 (2)	0.0358 (5)
H41	0.500 (3)	0.3563 (12)	0.058 (3)	0.043*
N42	0.3537 (3)	0.42254 (10)	−0.0869 (3)	0.0435 (6)
H42A	0.412 (4)	0.4577 (13)	−0.110 (3)	0.052*
H42B	0.262 (4)	0.4361 (13)	−0.060 (4)	0.052*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0298 (10)	0.0300 (10)	0.0239 (10)	0.0028 (8)	0.0031 (8)	−0.0014 (8)
N2	0.0341 (11)	0.0310 (10)	0.0265 (11)	0.0033 (8)	0.0006 (9)	−0.0032 (8)
C3	0.0260 (12)	0.0287 (11)	0.0264 (12)	−0.0016 (9)	0.0022 (10)	0.0004 (9)
C4	0.0274 (12)	0.0288 (11)	0.0266 (12)	−0.0023 (9)	0.0027 (10)	0.0022 (9)
C5	0.0289 (12)	0.0277 (11)	0.0317 (13)	0.0018 (10)	0.0040 (10)	0.0021 (10)
C11	0.0265 (12)	0.0319 (12)	0.0238 (12)	−0.0003 (9)	0.0040 (10)	0.0010 (9)
C12	0.0356 (14)	0.0342 (13)	0.0306 (13)	0.0061 (11)	0.0006 (11)	0.0018 (10)
C13	0.0401 (14)	0.0369 (13)	0.0316 (14)	0.0014 (11)	0.0055 (11)	−0.0053 (11)
C14	0.0286 (13)	0.0412 (13)	0.0235 (12)	−0.0034 (10)	0.0010 (10)	0.0028 (10)
C15	0.0371 (14)	0.0356 (13)	0.0337 (14)	0.0078 (11)	−0.0011 (11)	0.0040 (11)

C16	0.0387 (14)	0.0325 (12)	0.0325 (13)	0.0055 (11)	0.0035 (11)	−0.0036 (10)
O14	0.0503 (11)	0.0495 (11)	0.0273 (9)	0.0030 (9)	−0.0051 (8)	−0.0007 (8)
C141	0.0546 (18)	0.0587 (18)	0.0313 (14)	−0.0021 (14)	0.0016 (13)	−0.0058 (13)
C31	0.0289 (13)	0.0281 (12)	0.0296 (13)	−0.0025 (10)	0.0018 (10)	0.0001 (10)
O31	0.0433 (10)	0.0387 (10)	0.0340 (10)	0.0029 (8)	−0.0103 (8)	−0.0066 (7)
N31	0.0417 (12)	0.0299 (10)	0.0309 (11)	0.0056 (9)	−0.0018 (9)	−0.0036 (9)
N32	0.0701 (17)	0.0366 (13)	0.0440 (14)	0.0127 (12)	0.0003 (12)	−0.0093 (11)
C41	0.0297 (12)	0.0311 (12)	0.0288 (13)	0.0003 (10)	0.0050 (10)	0.0024 (10)
O41	0.0640 (12)	0.0331 (9)	0.0364 (10)	0.0141 (8)	0.0030 (9)	0.0014 (8)
N41	0.0391 (12)	0.0367 (11)	0.0274 (11)	0.0063 (9)	−0.0022 (9)	0.0022 (9)
N42	0.0436 (14)	0.0509 (14)	0.0314 (12)	0.0039 (11)	−0.0019 (10)	0.0086 (10)

Geometric parameters (Å, °)

N1—N2	1.349 (2)	C15—H15	0.9300
N1—C5	1.351 (3)	C16—H16	0.9300
N1—C11	1.431 (3)	O14—C141	1.422 (3)
N2—C3	1.333 (3)	C141—H14A	0.9600
C3—C4	1.424 (3)	C141—H14B	0.9600
C3—C31	1.485 (3)	C141—H14C	0.9600
C4—C5	1.380 (3)	C31—O31	1.249 (3)
C4—C41	1.482 (3)	C31—N31	1.317 (3)
C5—H5	0.9300	N31—N32	1.412 (3)
C11—C12	1.369 (3)	N31—H31	0.87 (3)
C11—C16	1.387 (3)	N32—H32A	0.97 (3)
C12—C13	1.394 (3)	N32—H32B	1.00 (3)
C12—H12	0.9300	C41—O41	1.236 (3)
C13—C14	1.381 (3)	C41—N41	1.325 (3)
C13—H13	0.9300	N41—N42	1.412 (3)
C14—O14	1.371 (3)	N41—H41	0.95 (3)
C14—C15	1.382 (3)	N42—H42A	0.95 (3)
C15—C16	1.377 (3)	N42—H42B	0.83 (3)
N2—N1—C5	111.78 (17)	C15—C16—C11	119.8 (2)
N2—N1—C11	119.05 (17)	C15—C16—H16	120.1
C5—N1—C11	129.07 (18)	C11—C16—H16	120.1
C3—N2—N1	105.65 (17)	C14—O14—C141	117.50 (19)
N2—C3—C4	110.88 (19)	O14—C141—H14A	109.5
N2—C3—C31	117.06 (19)	O14—C141—H14B	109.5
C4—C3—C31	132.06 (19)	H14A—C141—H14B	109.5
C5—C4—C3	104.01 (18)	O14—C141—H14C	109.5
C5—C4—C41	121.8 (2)	H14A—C141—H14C	109.5
C3—C4—C41	134.0 (2)	H14B—C141—H14C	109.5
N1—C5—C4	107.67 (19)	O31—C31—N31	122.0 (2)
N1—C5—H5	126.2	O31—C31—C3	122.5 (2)
C4—C5—H5	126.2	N31—C31—C3	115.47 (19)
C12—C11—C16	120.2 (2)	C31—N31—N32	122.4 (2)
C12—C11—N1	120.81 (19)	C31—N31—H31	120.9 (17)

C16—C11—N1	118.97 (19)	N32—N31—H31	116.0 (17)
C11—C12—C13	119.8 (2)	N31—N32—H32A	109.5 (17)
C11—C12—H12	120.1	N31—N32—H32B	108.1 (16)
C13—C12—H12	120.1	H32A—N32—H32B	110 (2)
C14—C13—C12	120.2 (2)	O41—C41—N41	122.8 (2)
C14—C13—H13	119.9	O41—C41—C4	120.6 (2)
C12—C13—H13	119.9	N41—C41—C4	116.59 (19)
O14—C14—C13	124.7 (2)	C41—N41—N42	123.4 (2)
O14—C14—C15	115.8 (2)	C41—N41—H41	118.0 (15)
C13—C14—C15	119.5 (2)	N42—N41—H41	118.6 (15)
C16—C15—C14	120.5 (2)	N41—N42—H42A	109.1 (16)
C16—C15—H15	119.7	N41—N42—H42B	107 (2)
C14—C15—H15	119.7	H42A—N42—H42B	101 (3)
C5—N1—N2—C3	0.2 (2)	C12—C13—C14—C15	−0.3 (3)
C11—N1—N2—C3	−176.56 (18)	O14—C14—C15—C16	179.4 (2)
N1—N2—C3—C4	0.2 (2)	C13—C14—C15—C16	−0.4 (4)
N1—N2—C3—C31	179.81 (18)	C14—C15—C16—C11	0.8 (4)
N2—C3—C4—C5	−0.6 (2)	C12—C11—C16—C15	−0.5 (3)
C31—C3—C4—C5	179.9 (2)	N1—C11—C16—C15	178.0 (2)
N2—C3—C4—C41	175.1 (2)	C13—C14—O14—C141	0.1 (3)
C31—C3—C4—C41	−4.4 (4)	C15—C14—O14—C141	−179.6 (2)
N2—N1—C5—C4	−0.6 (2)	N2—C3—C31—O31	168.0 (2)
C11—N1—C5—C4	175.8 (2)	C4—C3—C31—O31	−12.5 (4)
C3—C4—C5—N1	0.7 (2)	N2—C3—C31—N31	−11.1 (3)
C41—C4—C5—N1	−175.66 (19)	C4—C3—C31—N31	168.4 (2)
N2—N1—C11—C12	173.8 (2)	O31—C31—N31—N32	3.9 (4)
C5—N1—C11—C12	−2.3 (3)	C3—C31—N31—N32	−177.0 (2)
N2—N1—C11—C16	−4.7 (3)	C5—C4—C41—O41	6.1 (3)
C5—N1—C11—C16	179.2 (2)	C3—C4—C41—O41	−169.0 (2)
C16—C11—C12—C13	−0.2 (3)	C5—C4—C41—N41	−175.2 (2)
N1—C11—C12—C13	−178.6 (2)	C3—C4—C41—N41	9.8 (4)
C11—C12—C13—C14	0.6 (4)	O41—C41—N41—N42	−0.8 (4)
C12—C13—C14—O14	180.0 (2)	C4—C41—N41—N42	−179.5 (2)

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N31—H31 \cdots O31 ⁱ	0.88 (2)	2.04 (2)	2.851 (3)	153 (2)
N32—H32A \cdots O14 ⁱⁱ	0.97 (3)	2.58 (3)	3.256 (3)	127 (2)
N32—H32B \cdots N42 ⁱ	1.00 (2)	2.34 (3)	3.317 (3)	165 (2)
N41—H41 \cdots O31	0.95 (3)	1.78 (3)	2.714 (3)	166 (2)
N42—H42A \cdots O41 ⁱⁱⁱ	0.95 (3)	2.21 (3)	3.120 (3)	162 (2)
N42—H42B \cdots Cg1 ^{iv}	0.83 (3)	2.85 (3)	3.442 (3)	130 (2)
C5—H5 \cdots O41 ^v	0.93	2.40	3.314 (3)	166
C12—H12 \cdots O41 ^v	0.93	2.44	3.354 (3)	168

Symmetry codes: (i) $x+1/2, -y+1/2, z+1/2$; (ii) $x-1/2, -y+1/2, z-3/2$; (iii) $-x+1, -y+1, -z$; (iv) $x-1, y, z-1$; (v) $-x+1, -y+1, -z+1$.